Statistical Mechanics: Lecture A0

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▬▬ Phase Transitions

The phase of a thermodynamic system is characterized by its macroscopic properties. Those properties could be physical, electrical, magnetic or something else. For example, water can exist in three phases, solid, liquid and gas. The three phases of water can easily be characterized by the density - the densities of ice, water and vapour are widely different. Iron could exist in a phase where it is magnetized, and acts as a magnet, or it may exist in a phase where it is not magnetized, what we call the paramagnetic phase. Most metals can behave as a normal conductor and superconductor, in different situations. These are again, two different phases of the same metal. There are numerous other examples where systems can exist in different phases.

Under certain conditions, a system may make a transition from one phase to another. For example, water may freeze to form ice, iron may become magnetized from a non-magnetized phase, $Y_{1.2}Ba_{0.8}CuO_4$, which is metallic, becomes superconducting below $93°$K. These phenomena are called phase transitions.

All these transitions are driven by temperature, and have a *transition temperature* associated with them. However, all such phenomena need not be temperature driven. For example, recently some researchers have claimed to show that hydrogen goes from being an insulator to being a metal, under extremely high pressures. Thus phase transitions may be driven by pressure, or something else too. Nevertheless, temperature-driven phase transitions remain the most interesting ones. Phase transitions are the most interesting thermodynamic phenomena, and their study has become a separate area of research.

Examples of phase transition

Examples of phase transitions abound in nature. The most common have been already mentioned above.

Isotropic-nematic transition in liquid crystals

In liquid crystals, the molecules are highly elongated, roughly rod-shaped. At high temperatures, the material behaves like a liquid where molecules change their positions continuously, and the rods are radomly oriented. This is called the *isotropic phase*. At lower temperatures, liquid crystals go into a *nematic phase* where although the rod-shaped molecules are free to change their positions, they are roughly aligned

parallel to each other.

Order-disorder transitions in binary alloys

A well known example is β-brass, an alloy of copper and zinc, which has equal number of Cu and Zn atoms. Below $900°$C it is a solid, but the Cu and Zn atoms are arranged on a bcc lattic with no preferential arrangement of Cu and Zn atoms. As the solid is cooled to below $460°$C, it undergoes a transition to a phase where the Cu and Zn atoms sit on two different sublattices in a bcc lattice. Although the lattice structure of the solid does not change in this transition, an ordering of atoms takes place.

Liquid-solid transition

The freezing transition is the most commonly seen example of phase transtion. Any liquid shows an ordered arrangement of atoms only on a short scale. On a long distance scale, atoms are not arranged in any ordered fashion. However, as the temperature is lowered, the liquid freezes into a crystalline solid where atoms are arranged on a periodic lattice, and show long-range order. The two phases are generally characterized by two very different densities.

Phase separation in oil-water mixture

When oil and water a mixed together, they form a homgeneous mixture at high temperatures. However, as the temperature is lowered, below a transition temperature, oil and water start separating out into oil-rich and water-rich regions.

▬▬ Characteristics of phase transitions

Fluctuations

Phase transitions are typically associated with fluctucations in certain quantities becoming very large. For example, we learnt that fluctuations in the energy of a system, in canonical ensemble, are very small in the thermodynamic limit. Which means that the energy remains practically constant. This property breaks down near a paramagnetic to ferromagnet phase transition. Density of a binary liquid is almost uniform at higher temperatures. As the temperature is lowered, and approaches the transition temperature, there are large fluctuations in the density of the mixture. The density fluctuates at length scales of the wavelength of light, thus scattering the light which would have ordinarily passed through unaffected. This results in the transparent liquid becoming cloudy, a phenomenon called *critical opalescence*. Critical opalescence can

also be seen in boiling liquids.

Divergent susceptibility

Susceptibility is generally described as the response of the system to an external "force". For example, response of magnetization to an external magnetic field is related to magnetic susceptibility. Response of a gas to an external pressure is related to it's compressibility. Compressibility is also a kind of susceptibility. Response electric polarizations of a dilectric , in response to an external electric field, is related to it's electric susceptibility. Near transition temperature, susceptibility becomes very large. For example, when as gas is about to condense into liquid, it becomes highly compressible. A small increase in pressure, leads to a large change in volume.

Symmetry breaking

Very often there are situations where above the transition temperature (T_c) the system shows some symmetry, and below T_c that symmetry is spontaneously broken, without any external field. For example, in the paramagnetic phase the magnet has rotational symmetry. Even the Hamiltonian is rotationally invariant. However, below T_c them magnetic moments of the atoms align in a particular direction, thus breaking rotational symmetry. This happens even without any

external magnetic field. In liquids, there is a translational symmetry. But when the liquid freezes into a crystalline solid, this symmetry is broken. It reduces to a discrete translational symmetry. In binary mixtures too, there is a translational symmetry at higher temperatures, but when the mixture separates into two phases, the translational symmetry is broken. CP-symmetry (or charge conjugation parity symmetry) states that physical laws should be the same if a particle is interchanged with its antiparticle (C symmetry) while its spatial coordinates are inverted ("mirror" or P symmetry). It is believed that if CP symmetry was preserved at the time of the big bang, an equal amount of matter and anti-matter should have been produced. But today we only see matter in abundance, and not anti-matter. So somewhere during the course of evolution of the universe, a phase transition must have occured where this CP symmetry was broken.

Breakdown of ergodicity

A phase transition is also associated with the breakdown of ergodicity, which means the system doesn't visit all regions of phase space in any finite time. In fact, symmetry breaking is a special case of breakdown of ergodicity. We will come back to this aspect of phase transitions while studying the Ising model.

Order parameter

An averaged, macroscopic quantity can be identified for every phase-transition, which has very different values in two difference phases. This quantity is called the *order parameter*. Typically, the order parameter is zero above the transition temperature (T_c), and non-zero below it. Order parameter plays a central role in the study of phase transitions. However, the order parameter may not always be physically observable. The name probably stems from the fact that in many phase transitions, one phase has lower symmetry, and thus more order. Following are some examples of phase transitions and the order parameters associated with them.

Transition	Example	Order parameter
Ferromagnetic	Iron	magnetization
Anti-ferromagnetic	MnO	magnetization of a sublattice
Liquid-gas	Water	$\rho - \rho_g$ (density - density-in-gas-phase
Ferroelectric	$BaTiO_3$	magnetization
Superconductivity	many metals	$|\Psi|^2$ (density of superconducting electrons)
Liquid crystals	Soap-Water mixture	$\langle \frac{1}{2}(2\cos^2\theta - 1)\rangle$ (θ is an angle related to orientation of rod molecule)
Phase separation	Oil-water	local density

▬▬ Classification of phase transitions

Phase transitions are generally characterized by large changes in the behavior of various thermidynamic potentials. Where one is dealing with systems with fixed volume, e.g. in magnetic phase transitions, one may look at **Hemlholtz free energy** $F = U - TS$. In the situations where the volume does not remain constant, e.g. in liquid-solid phase transitions, one should look at **Gibbs free energy** $G = U - TS + PV$.

Ehrenfest's criterion

Eherenfest characterized phase transition based on the discontinuity in various derivatives of free energy:

First order: transitions in which there is a discontinuity in the first derivative of free energy with respect to temperature, just above and below T_c, i.e.,

$$\left.\frac{\partial F}{\partial T}\right|_{T_{c-}} \neq \left.\frac{\partial F}{\partial T}\right|_{T_{c+}}.$$

First derivative of Hemlholtz free energy is virtually entropy $S = -(\frac{\partial F}{\partial T})_V$. If $\frac{\partial F}{\partial T}$ is discontnuous across the transition, it means there is an entropy change ΔS across the transition. This change corresponds to a heat which is generated or absorbed across the transition, $Q = T\delta S$.

Second order: transitions in which the first derivative of free energy is continuous across the transition, but there is a discontinuity in the second derivative of free energy just above and below T_c, i.e.,

$$\left.\frac{\partial^2 F}{\partial T^2}\right|_{T_{c-}} \neq \left.\frac{\partial^2 F}{\partial T^2}\right|_{T_{c+}}.$$

Similarly n'th order phase transition is defined as one in which the n'th derivative of the free energy is discontinuous at T_c, $\frac{\partial^n F}{\partial T^n}|_{T_{c-}} \neq \frac{\partial^n F}{\partial T^n}|_{T_{c+}}$. Ehrenfest criterion

works reasonably well to describe many first and second order phase transitions. However, there are many phase transitions which don't quite fit in Ehrenfest's classification.

Modern classification

Modern classification is quite similar to Ehrenfest's classification. However, the phase transitions are assumed to be only of two kinds: **first order transitions** and **continuous phase transitions**. This classification depends on whether the first derivative of free energy is continuous across the transition or not. If it is not continuous, it is called a first order transition, if it is continuous, it is called a continuous phase transition. Another way of saying the same thing is that if there is a latent heat involved, it is a first order transition, otherwise it is a continuous transition. Quite often, the name "2nd order" is used for continuous phase transitions. However, it does not mean that one is following the Ehrenfest criterion - the name is just a relic from the older classification.

First order transitions are also characterized by a discontinuous jump in the order parameter at T_c. In continuous phase transitions, the order parameter increases from zero as one goes below T_c. For example, in freezing of water to ice, the density takes a sudden jump

at the freezing temperature. That is an example of a first order transition. On the other hand, in a ferromagnet, as one goes below T_c, magnetization gradually increases from zero to non-zero values. That is a continuous phase transition.

Critical phenomena and universality

Critical exponents

In different phase transitions, even of the same kind, the transition temperature T_c varies from material to material. This is intuitively obvious because it depends on the microscopic details of the interaction between atoms and molecules. However, it is observed that the behavior of materials, in close vicinity of the transition, is very closely similar. Most properties which are affected by the phase transition, scale as a power of $|T - T_c|$. The powers of $|T - T_c|$ which arise, are called *critical exponents*. The table below lists the critical exponents for magnetic and liquid-gas transitions.

| **Magnetic transition**	
Specific heat	$C \sim |T - T_c|^{-\alpha}$
Magnetization	$M \sim (T_c - T)^{\beta}$
Susceptibility	$\chi \sim |T - T_c|^{-\gamma}$
Critical isotherm ($T = T_c$)	$B \sim |T - T_c|^{\delta}$
Correlation length	$\xi \sim |T - T_c|^{-\nu}$

Liquid-gas transition	
Specific heat	$C_V \sim |T - T_c|^{-\alpha}$
Density diff	$\rho - \rho_g \sim (T_c - T)^{\beta}$
Isothermal compressibility	$\kappa_T \sim |T - T_c|^{-\gamma}$
Critical isotherm ($T = T_c$)	$P - P_c \sim |\rho - \rho_g|^{\delta}$
Correlation length	$\xi \sim |T - T_c|^{-\nu}$

Universality

Now, the exponents of two quantities in two different phase transitions, are given the same symbol in the table above. For example, there is no a priori reason to believe that the β occuring in magnetization has anything two do with the β occuring in $\rho - \rho_g$, in liquid-gas transition. However, studies of liquid-gas transitions show that the various exponents have universal values, which are independent of the nature of liquids. For example, the left figure below[1] shows the curve

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[1] EA Guggenheim, J.Chem.Phys. 13, 253 (1945)

where the liquid and gas phase coexists, for four different liquids. When plotted in the rescaled variables T/T_c and ρ/ρ_c, they all lie on the same curve! This shows that behavior of various liquids near criticality, is universal.
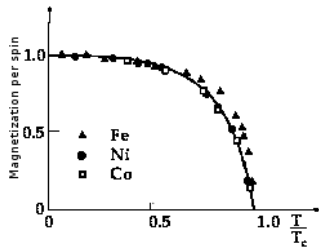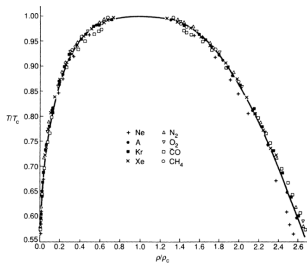
The figure on the right above, shows the magnetization per spin, plotted against the rescaled temperature T/T_c, for three ferromagnetic materials. In these rescaled variables, the experimental data for Fe, Ni and Co, all approximately lie on the same curve. This is so inspite of the fact that the T_c for these three metals are quite different. The curve corresponds to $M \sim |T_c - T|^{1/3}$. Thus the value of the critical exponent β comes out to be 1/3, independent of the magnetic material.

What is a bigger surprise than this is the fact that in the plot on the left above, which describes liquid-gas transitions, the theoretical curve which fits the data well, corresponds to $\rho_l - \rho_g \sim |T_c - T|^{1/3}$. This means

the critical exponent β is universal for liquid-gas and ferromagnetic phase transitions. This clearly indicates that the behavior of various quantities, near criticality, is universal. Other critical exponents have been experimentally measured and the universality is reinforced. Various critical exponents are not independent, as one might presume, and certain inequalities for them can be proven. Two of them are shown below:

$$\alpha + 2\beta + \gamma \geq 2, \qquad \alpha + \beta(1 + \delta) \geq 2.$$

One now arrives at the conclusion that there is a universality associated with various physical quantities in the vicinity of the phase transition. Individual details of the system, and even the nature of phase transition are unimportant. This universality also suggests that when theoretically modeling phase transitions, the details of the model may not be important for describe the critical behavior. It may be that a model which is very simple, may be able to capture the behavior of a phase transition which has complex microscopic interactions underlying its dynamics. As we shall see later, a very simple spin model is able to describe a wide variety of phase transitions.